


PAPER • OPEN ACCESS

## Manufacture of optical ceramics based on two solid solutions of the AgBr – (TlBr<sub>0.46</sub>I<sub>0.54</sub>) system

To cite this article: L V Zhukova *et al* 2020 *J. Phys.: Conf. Ser.* **1695** 012106


View the [article online](#) for updates and enhancements.



The Electrochemical Society  
Advancing solid state & electrochemical science & technology  
2021 Virtual Education

**Fundamentals of Electrochemistry:**  
Basic Theory and Kinetic Methods  
Instructed by: **Dr. James Noël**  
Sun, Sept 19 & Mon, Sept 20 at 12h–15h ET

Register early and save!



# Manufacture of optical ceramics based on two solid solutions of the $\text{AgBr} - (\text{TlBr}_{0.46}\text{I}_{0.54})$ system

L V Zhukova<sup>1\*</sup>, A E Lvov<sup>1</sup>, D D Salimgareev<sup>1</sup>, A A Yuzhakova<sup>1</sup>,  
D A Belousov<sup>1</sup>, M S Korsakov<sup>1</sup>

<sup>1</sup>Department of chemical technology, Ural federal university named after the first President of Russia B. N. Yeltsin, Ekaterinburg 620002, Russia

\*l.v.zhukova@urfu

**Abstract.** This work is devoted to the synthesis and the optical properties study of a new multicomponent heterophase ceramic based on two solid solutions of the  $\text{AgBr} - (\text{TlBr}_{0.46}\text{I}_{0.54})$  system. Ceramics are transparent in the infrared range from 1.0 to  $40.0 \div 50.0 \mu\text{m}$ , non-hygroscopic, are photo- and radiation-resistant, flexible, as a result of which various optical products are made from it by hot embossing.

## 1. Introduction

Today, there is a wide development of the mid-infrared range, since it is deficiently studied and poorly developed. This is evidenced by a very limited number of existing solid-state and fiber laser systems capable of generating radiation in this range. Therefore, a popular area is the creation of multifunctional elements based on crystalline ceramics for the generation, transmission, recording and control of infrared (IR) radiation in a wide spectral range from 1.0 to 50.0 microns. However, the known ceramic materials have complex manufacturing techniques and require special expensive equipment. In addition, their transparency range is limited by the visible and near infrared ranges.

## 2. Raw materials synthesis

The technology for obtaining optical ceramics is based on the hydrochemical method, similar to the production of materials for single crystals, which we called thermozone crystallization-synthesis (TZKS)[1]. The method essence is the recrystallization of individual sparingly soluble metal halides in acid solutions. By creating a temperature gradient in the reactor zones, we obtain a concentration dissolved ions gradient (the solubility of halides increases with growth temperature). Thus, two zones are formed: the elevated temperature zone, in which the solution is saturated, and the lower temperature (crystallization) zone, in which the saturated solution is cooled, the solubility of metal halides decreases, respectively, the solution is saturated and precipitates (Figure 1). The continuous circulation of the solution from the saturation zone to the crystallization zone is due to natural convection, since heat is supplied to the reactor bottom and heat is removed to the top. Thus, when controlling the temperature gradient in the reactor, we monitor, firstly, the convective flow rate and, therefore, the recrystallization rate, and secondly, the composition of the crystallized material, since different metal halides have varying temperature solubilities.

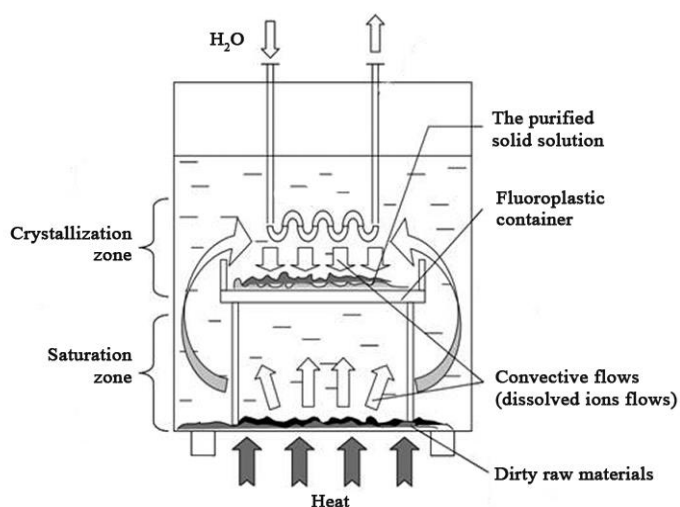
The solubility and crystallization of monovalent thallium and silver halides in hydrohalic acids aqueous solutions over a wide temperature range are considered in detail in [2].



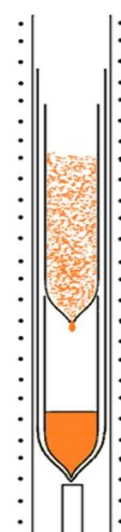
The TZKS method makes it possible to stably obtain high-purity raw materials from cationic impurities (99.9999 wt.% and more) due to the most of the impurities remain in the acid solution. It is important to note that the TZKS method is easily scalable and can be successfully implemented both at the laboratory and at the industrial level. The method has proved itself in all technological respects as simple, cost-effective (since it does not require expensive equipment), energy-saving (due to low synthesis temperatures), and environmentally friendly (since it ensures the organization of the process with minimal waste in a closed cycle).

### 3. Ceramics growth

Two-phase ceramics of the  $\text{AgBr} - (\text{TlBr}_{0.46}\text{I}_{0.54})$  system are grown by the vertical method of directed crystallization from melt in ampoules made of Pyrex glass. To improve the grown ceramics quality, the piercing method is used (Figure 2), for which two ampoules are applied, located one above the other. The upper ampoule filled with the raw material has a small hole in the lower part, at a temperature of 470–480 °C the raw material is melted, then the melt capillary filtration process into the second ampoule takes place. This process makes it possible to reduce the amount of air bubbles trapped by the melt, the natural removal of which would be difficult due to the sufficiently high viscosity of the melt. After completion of the capillary filtration process, the second ampoule begins to be moved at a speed of 3–30 mm/h to the lower zone of the installation, having a temperature 250–260 °C. In the conical part of the second ampoule, composite structures crystallize based on the cubic (Fm3m) and rhombic phases (R-3) of silver halides and monovalent thallium solid solutions.



**Figure 1.** Thermal zone crystallization-synthesis (TZKS) method scheme.

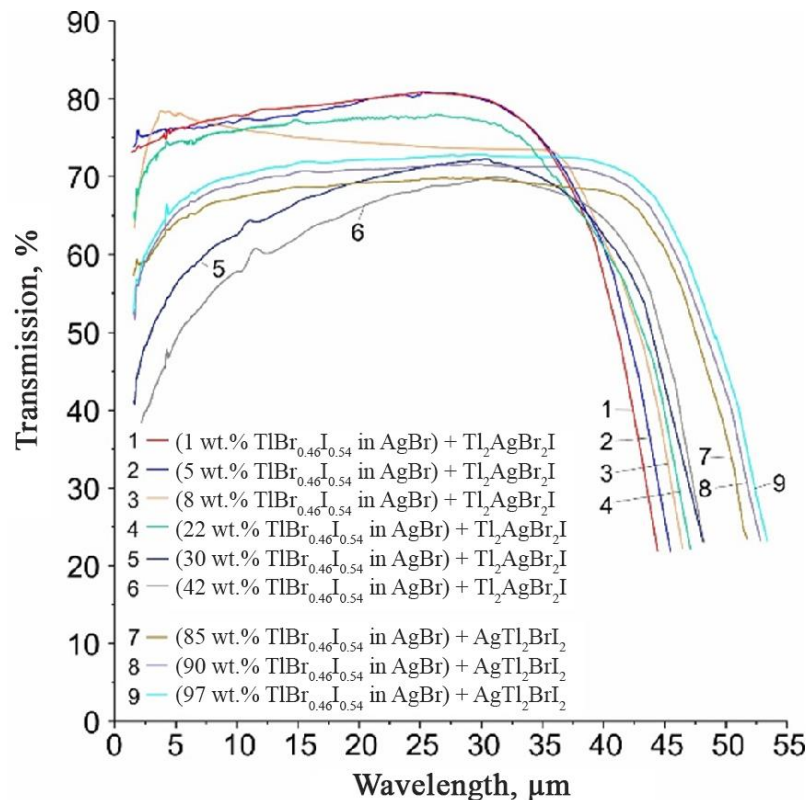


**Figure 2.** The capillary filtration process with the ceramics growth

### 4. Optical properties

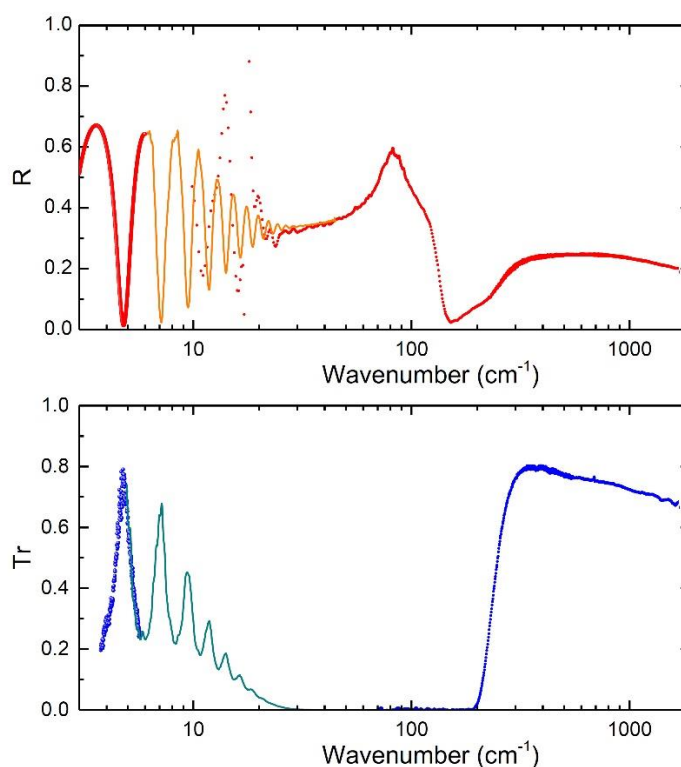
To date, the article's authors for the first time synthesized a multicomponent, highly transparent, without absorption windows in the range from 1.0 to 40.0 ÷ 50.0 μm (Figure 3) heterophase ceramic based on cubic and rhombic phases two solid solutions. The ceramic is based on the cubic phase of the  $\text{AgBr} - (\text{TlBr}_{0.46}\text{I}_{0.54})$  system with a  $\text{TlBr}_{0.46}\text{I}_{0.54}$  content in  $\text{AgBr}$  from 1.0 to 42.0 wt. % and from 85.0 to 97.0 wt. %, which follows from the previously studied diagram of the system' melting point [3]. For the first region, the rhombic phase has the composition  $\text{Tl}_2\text{AgBr}_2\text{I}$ , and for the second,  $\text{AgTl}_2\text{BrI}_2$ , which is confirmed by studies. It should be noted that the obtained ceramics' quality and the ratio of solid crystalline phases in it depend primarily on the degree of starting components' homogenization, and to a much lesser extent on the growth rate.

The main optical materials characteristic is their transparency range. The spectral range of the new ceramics was studied on plane-parallel plates from 300 to 1000 nm thick, manufactured on a Specac 15 ton manual hydraulic press by hot embossing. The plates corresponded to different compositions of AgBr – (TlBr<sub>0.46</sub>I<sub>0.54</sub>) system' solid solutions. The ceramics spectral transmission was determined using IR-Fourier spectrometers IRPrestige-21 (Shimadzu) operating in the spectral range 7800 – 240 cm<sup>-1</sup> (1.28 – 41.70 μm) with various combinations of detectors and dividers, VERTEX 80 (Bruker) with an expanded IR range 680 – 165 cm<sup>-1</sup> (from 14.7 to 60.6 μm).



**Figure 3.** Transmission spectra of multicomponent heterophase ceramics based on two solid solutions of the AgBr – (TlBr<sub>0.46</sub>I<sub>0.54</sub>) system.

In addition to the transmission study in the infrared region, an investigation was made of the transmission and reflection spectra at terahertz frequencies. Samples were made using hot embossing technology. The resulting samples were 0.4-0.5 mm thick and about 15 mm in diameter. The plates had a high degree of parallelism. Spectral measurements were carried out using the Epsilon submillimeter spectrometer. The following data were obtained: the phonon frequency was 77.5 cm<sup>-1</sup>, the contribution of the phonon-dielectric was 6.2, the extinction coefficient was 18 cm<sup>-1</sup>, and the oscillations were anharmonic (Figure 4). The transmission range in the mid-infrared range has a plateau profile, and the transmission edge in the long wavelength range is about 260 cm<sup>-1</sup>. Peak bandwidths can be observed in the terahertz range.



**Figure 4.** Reflection spectra (above) and transmission (below) at terahertz frequencies for sample 22 wt. % AgI in AgBr.

The synthesized ceramics are highly transparent, flexibility, non-hygroscopicity, photo- and radiation-resistant [4, 5], while the method for its preparation consists one step (the vertical method of directional crystallization), therefore it is an economical and practically waste-free process. The targeted synthesis of heterophase optical ceramics based on the AgBr – (TlBr<sub>0.46</sub>I<sub>0.54</sub>) system can significantly simplify and reduce material and time costs, in comparison with the growing crystals' process of the same system. In addition, due to the ceramics flexibility, it is suitable for the manufacture by hot embossing of various optical products [6].

### Acknowledgments

This work was supported by the Russian Science Foundation under grant No. 18-73-10063.

### References

- [1] Zhukova L V, Korsakov A S, Salimgareev D D, 2015 *Infrared crystals. Theory and practice: a textbook* (Ekaterinburg: UMTS UPI) p 215.
- [2] Zelyanskii A V, Zhukova L V, Kitaev G A, 2001 *Solubility of AgCl and AgBr in HCl and HBr* (*Inorg. Mater.* vol 37 N 5) pp 523-526
- [3] Salimgareev D D, Lvov A E, Korsakova E A, et al 2019, *Mater. Today Commun.* vol 20 p 100551
- [4] Korsakov A, Salimgareev D, Lvov A, et al 2016 *Opt. Mater.* vol 62 pp 534-537
- [5] Korsakova E, Lvov A, Salimgareev D, et al 2018, *Infrared Phys. and Tech.* vol 93 pp 171-177
- [6] Korsakov A S, Vrublevsky D S, Korsakov V S, et al 2015 *Appl. Opt.* vol 26 pp 8004-8009